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(54) Title: SILANE TREATMENTS FOR CORROSION RESISTANCE AND ADHESION PROMOTION

(57) Abstract

A method of treating a substrate by applying a coating of a silane solution comprising at least one bis-silyl aminosilane which has been at least partially hydrolyzed and at least one bis-silyl polysulfur silane which has been at least partially hydrolyzed. The silane coating provides corrosion resistance, as well as improved adhesion to electrocoats and other polymers. Silane coated substrates, as well as a silane solution, are also provided.

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SILANE TREATMENTS FOR CORROSION RESISTANCE AND ADHESION PROMOTION

Field of the Invention

The present invention relates to silane coatings. More particularly, the invention relates to silane coatings for increasing corrosion resistance in metals and/or improving bonding of metals to polymers, ceramics to polymers and glass to polymers.

Description of Related Art

Many metal surfaces are electrocoated in order to not only protect the metal surface, but also to provide an aesthetically-pleasing appearance. Electrocoating (also referred to as "E-coat") is an electrochemical process by which an organic coating is applied to a metal using electrical current. The metal article (or substrate) to be coated is immersed in a bath containing the electrocoat material, and a D.C. current is applied to the bath. The workpiece (i.e., the metal article to be coated) acts as one electrode (usually the cathode), and a second electrode is provided in the bath (typically the electrodialysis cell itself) acts as the second electrode. The electrically charged particles of the coating material will migrate to the oppositely-charged electrode (i.e., the workpiece), and are deposited thereon. The organic coatings used in electrocoating processes are typically paints or primers.

Metal used in the automobile industry are typically electrocoated with a primer prior to painting. Such automotive metals include cold rolled steel ("CRS"), electrogalvanized steel ("EGS"), hot dipped galvanized steel ("HDG"), galvanneal (annealed hot-dipped galvanized steel), aluminum and aluminum alloys, and other zinc-alloy coated metals. In order to improve adhesion of the electrocoat to the metal surface, the metal is typically treated with a zinc phosphate conversion coating. Zinc phosphate conversion coatings typically require a chromate rinse which is environmentally undesirable, and must be modified with fluorides when used on aluminum surfaces.

Recently, various techniques for eliminating the use of chromate have been proposed. In particular, various silane coatings have been developed for preventing corrosion of metal substrates. For example, U.S. Patent No. 5,108,793 describes a technique of coating certain metal substrates with an inorganic silicate followed by treating the silicate coating with an organofunctional silane (U.S. Patent No. 5,108,793). U.S. Patent No. 5,292,549 teaches the rinsing of metallic coated steel sheet with a solution containing an organic silane and a crosslinking agent. Other silane coatings are described in U.S. Patent Nos. 5,750,197 and 5,759,629, both of which are incorporated herein by way of reference.

Often, the corrosion protection provided by a particular silane coating will depend upon the identity of the metal substrate itself. In addition, the silane coating must also be compatible with any polymer layer to be applied over the silane coating (such as paints, adhesives or rubbers). For example, while a particular silane coating may provide excellent paint adhesion and corrosion protection, that same silane coating may provide little or no adhesion to certain rubbers. Thus, it is often necessary to tailor the silane coating to the specific application.

Various types of silanes have been shown to improve corrosion protection, and to provide improved adhesion between metals and polymers, glass and polymers and ceramics and polymers. Often, however, the type of silane used for optimal substrate-polymer adhesion is specific to the type of substrate and type of polymer employed. In addition, any treatment used prior to electrocoating must provide an electrically conductive coating which is also resistant to the harsh conditions of the electrocoat bath. For example, when cathodic electrocoating is used, any pretreatment coating must be resistant to a pH of about 10–12. While zinc phosphate conversion coatings are electrically conductive and can withstand the alkaline bath conditions, most silane films are insulators and may not withstand a high alkaline environment. An insulating film on the metal will result in poor quality electrocoat films which are of insufficient thickness and/or show cratering.

Thus, there is a need for a simple technique for treating a substrate prior to provide improved adhesion between the substrate and the polymer coating.

There is also a need for a simple technique for treating a metal substrate prior to electrocoating, particularly to improve corrosion performance, and provide improved adhesion between the metal and the electrocoat, and provide a high quality, uniform electrocoat.

It would be desirable to provide an improved method of treating a metal substrate in order to provide corrosion protection and/or improve adhesion to a polymer coating (such as paints or adhesives, particularly electrocoat paints).

It would also be desirable to provide a silane solution which may be applied to a metal substrate in order to provide corrosion protection and/or improve adhesion to a polymer coating (such as paints or adhesives, particularly electrocoat paints).

It would also be desirable to provide a silane solution which may be applied to a substrate in order to improve adhesion between glass and polymer coatings.

It would also be desirable to provide a silane solution which may be applied to a substrate in order to improve adhesion between ceramics and polymer coatings.

SUMMARY OF THE INVENTION

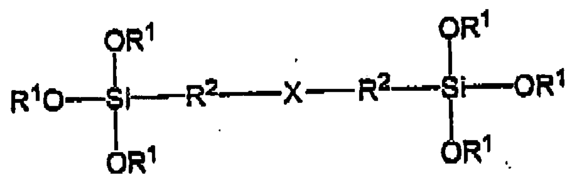
One aspect of the present invention provides a method of treating a metal substrate, comprising:

(a) applying a first coating of a silane solution onto the metal substrate, the silane solution comprising at least one silane which has been at least partially hydrolyzed, the silane chosen from the group consisting of bis-silyl aminosilanes and bis-silyl polysulfur silanes.

The silane coated metal substrate has improved corrosion resistance, even without subsequent painting or application of an other type of polymer coating (such as a paint, adhesive, plastic or rubber). The silane coating also

provides improved adhesion to polymer coatings, such as rubbers, adhesives and paints, particularly electrocoat paints.

Suitable bis-silyl aminosilanes for use in the present invention include:

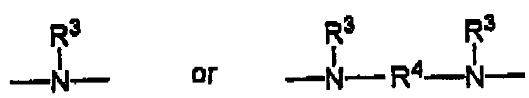


wherein:

each R^1 is individually chosen from the group consisting of: hydrogen, C_1 - C_{24} alkyl and C_2 - C_{24} acyl;

each R^2 is individually chosen from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups; and

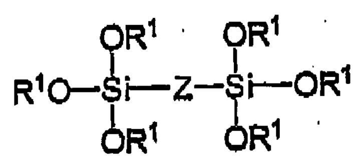
X is either:



wherein each R^3 is individually chosen from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and

R^4 is chosen from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups.

Suitable bis-silyl polysulfur silanes include:



wherein each R^1 is an alkyl or an acetyl group, and Z is —Q—S_x—Q—, wherein each Q is an aliphatic or aromatic group, and x is an integer of from 2 to 10.

The above methods may be used on a variety of metal substrates, including:

-a metal substrate having a zinc-containing coating;

-steel (e.g., cold rolled steel, hot rolled steel, coated steel and stainless steel);

-aluminum;

-aluminum alloys;

-zinc;

-zinc alloys;

-magnesium;

-magnesium alloys;

-copper;

-copper alloys;

-tin; and

-tin alloys.

In a further embodiment, the present invention also provides a silane solution comprising at least one substantially hydrolyzed bis-silyl aminosilane; and at least one substantially hydrolyzed bis-silyl polysulfur silane.

The silane treatment solution may be utilised in additional treatment methods to electrocoating. In particular, the treatment solution finds utility in methods of adhesion promotion between glass and polymers, and ceramics and polymers. Suitable polymer coatings include rubbers, adhesives plastics and paints.

Particular preferable plastic coatings include acrylic, polyester, polyurethane, polyethylene, polyimide, polyphenylene oxide, polycarbonate, polyamide, epoxy, phenolic, acrylonitrile-butadiene-styrene, and acetal plastics. Particular preferable rubber coatings include sulfur cured rubbers, nitrile rubbers, chloroprene rubbers, polyisoprenes, polybutadienes, siliicone rubbers

(including fluorosilicone rubbers), acrylic rubbers and isoprene-acrylonitrile rubbers.

The term ceramics generally include (but are not limited to) silica, alumina, silicon nitride, boron carbide and boron nitride.

The term glass generally includes (but is not limited to) soda glass, barium glass, strontium glass, borosilicate glass and glass-ceramics containing lanthanum.

Silane coated substrates, as well as metal substrates, including electrocoated metal substrates, are also provided by the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Applicants have found that the performance of an electrochemically applied coating (i.e., electrocoating) may be improved by applying a silane coating prior to electrocoating. The silane coating is applied from a silane solution which includes at least one bis-silyl aminosilane, at least one bis-silyl polysulfur silane, or a mixture of at least one bis-silyl aminosilane and at least bis-silyl polysulfur silane. The silane coating is applied from a solution wherein the silanes have been at least partially hydrolyzed. The silane undercoating provides corrosion protection which is at least equivalent to that provided by phosphate conversion coatings, and also provides excellent adhesion between the metal and the electrocoat. The electrocoat films (or coatings) are of the same thickness as those formed on phosphate conversion coatings, and are free of craters and other defects. In addition, the method of applying the silane coating is much simpler than phosphate conversion coating methods, and avoids the environmentally undesirable by-products of phosphate conversion coatings (such as chromium). The silane coatings of the present invention also provide improved corrosion protection, even without subsequent electrocoating, and provide adhesion to other polymer layers (such as non-electrocoat paints, rubbers and adhesives). Therefore, the present application is not limited to silane coatings for improving electrocoat adhesion.

The use of certain silane coatings for promoting adhesion and/or preventing corrosion of metal surfaces is known in the art. For example, Applicants have previously found that the corrosion of metal can be prevented by applying a treatment solution containing one or more hydrolyzed vinyl silanes to the metal, and that paint may be applied directly over the resulting silane coating (see U.S. Patent No. 5,759,629). While the corrosion protection and paint adhesion provided by the resulting vinyl silane coating was surprisingly superior to conventional chromate-based treatments, Applicants have found that vinyl silane coatings of the type described in their U.S. Patent No. 5,759,629 do not provide adhesion between the metal surface and an electrocoat equivalent to that provided by phosphate conversion coatings. Similarly, coatings applied to metal surfaces from aqueous solutions of 1,2-bis-(triethoxysilyl)ethane ("BTSE"), γ-ureidopropyltrialkoxysilane (γ-UPS), or N-[2-(vinylbenzylamino)-ethyl]-3-aminopropyltrimethoxysilane (SAAPS), do not improve the adhesion between a metal surface and an electrocoat. Thus, it is surprising and unexpected that a silane coating applied from a silane solution which includes at least one bis-silyl aminosilane, at least one bis-silyl polysulfur silane, or a mixture of at least one bis-silyl aminosilane and at least bis-silyl polysulfur silane provides excellent adhesion between a metal substrate and an electrocoating.

The solutions and methods of the present invention may be used on a variety of substrates. The substrates include metals, including zinc, zinc alloys, metal substrates having a zinc-containing coating, steel (e.g., cold rolled steel, hot rolled steel and stainless steel), aluminum, aluminum alloys, and magnesium alloys. The metal substrate can even be sandblasted prior to using the solutions and methods of the present invention. For example, a steel substrate (such as hot rolled steel) may be sandblasted prior to application of the solutions of the present invention. Sandblasting typically leaves a high surface roughness as well as surface contaminants, both of which create difficulties when one attempts to apply a coating to sandblasted substrates. The solutions and methods of the present invention, however, allow for the formation of silane coatings on sandblasted substrates.

The solutions and methods of the present invention are particularly useful on sheet metals used in the automotive industry, since such metals are often electrocoated. These automotive metals include: steel (particularly cold rolled steel ("CRS")); steel having a zinc-containing coating, such as galvanized steel (especially hot dipped galvanized steel ("HDG") and electrogalvanized steel ("EGS")), galvanneal (annealed hot dipped galvanized steel) and similar types of coated steel; zinc and zinc alloys, zinc-nickel alloy (typically about 5% to about 13% nickel content), and zinc-cobalt alloy (typically about 1% cobalt); aluminum; and aluminum alloys. The solutions of the present invention may also be used on a variety of other metals, such as GALVALUME® (a 55%-Al/43.4%-Zn/1.6% - Si alloy coated sheet steel manufactured and sold, for example, by Bethlehem Steel Corp) and GALFAN® (a 5%-Al/95%-Zn alloy coated sheet steel manufactured and sold by Weirton Steel Corp., of Weirton, WV).

The solutions of the present invention may be applied to the metal prior to shipment to the end-user, and even provide corrosion protection during shipment and storage (including the prevention of wet-storage stain such as white rust). The end user merely applies an electrocoating in the usual manner directly on top of the silane coating provided by the present invention. The silane coatings of the present invention not only provide excellent corrosion protection, but also provide superior adhesion between the metal substrate and the electrocoat. Thus, unlike many of the currently-employed treatment techniques, the silane coatings of the present invention need not be removed prior to electrocoating.

The solutions of the present invention comprise one or more bis-silyl aminosilanes, one or more bis-silyl polysulfur silanes, or a mixture of one or more bis-silyl aminosilanes and one or more bis-silyl polysulfur silanes. The solutions do not require the use or addition of silicates or aluminates, and eliminate the need for phosphate conversion coatings. The silanes in the treatment solution should be at least partially hydrolyzed, and are preferably substantially fully hydrolyzed. The silane solutions of the present invention preferably include water, and may include one or more compatible solvents

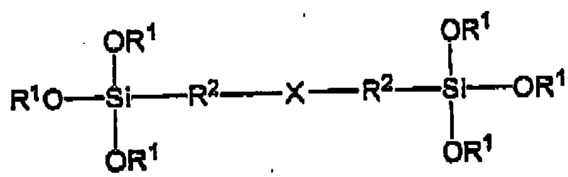
(such as ethanol, methanol, propanol or isopropanol), as needed. A solvent will generally be needed only if the solution includes a bis-silyl polysulfur silane (in order to solubilize the polysulfur silane). Thus, the amount of solvent needed will vary depending upon the amount (if any) of bis-silyl polysulfur silane(s) in the solution. As further detailed below, the ratio of water to solvent may be between about 1:99 and about 99:1, more preferably between about 1:1 and about 1:20.

Alternatively, the silanes (particularly the polysulfur silane(s)) may be prepared as an emulsion without a solvent. The silane(s) is simply mixed with water and a suitable surfactant known to those skilled in the art. A emulsified, hydrolyzed solution of a bis-silyl polysulfur silane can be prepared, for example, by mixing a 5% solution of the silane in water along with 0.2% of a surfactant (by volume). Suitable surfactants include, for example, sorbitan fatty acid esters (such as Span 20, available from ICI Surfactants). Once the emulsion of polysulfur silane has been prepared, it may simply be applied to the metal surface, or mixed with one or more bis-silyl aminosilanes as described below.

Although not critical, the application pH of the silane solution is preferably between about 3.5 and about 10. The term "application pH" refers to the pH of the silane solution when it is applied to the metal surface, and may be the same as or different from the pH during solution preparation. The pH may be adjusted by the addition of one or more acids, preferably organic acids such as acetic, formic, propionic or iso-propionic. Sodium hydroxide (or other compatible base) may be used, if needed, to raise the pH of the treatment solution. For silane solutions according to the present invention which do not contain bis-silyl polysulfur silanes, the preferred pH is between about 4 and about 9, most preferably between about 6 and about 9. When the silane solution according to the present invention does not contain a bis-silyl aminosilane, the preferred pH is between about 3.5 and about 10, most preferably between about 6 and about 9. When the silane solution of the present invention includes both a bis-silyl aminosilane and bis-silyl polysulfur silane, the preferred application pH is between about 4 and about 9, most preferably between about 8 and about 9

(particularly when used to improve electrocoat adhesion). It should be pointed out that pH adjustment is not always necessary, since many of the silanes used in the present invention have a natural pH in an aqueous solution which falls within the preferred ranges mentioned above.

The preferred bis-silyl aminosilanes which may be employed in the present invention have two trisubstituted silyl groups, wherein the substituents are individually chosen from the group consisting of hydroxy, alkoxy, aryloxy and acyloxy. Thus, these bis-silyl aminosilanes have the general structure:



wherein each R^1 is chosen from the group consisting of: hydrogen, C_1 - C_{24} alkyl (preferably C_1 - C_6 alkyl), and C_2 - C_{24} acyl (preferably C_2 -C_4 acyl). Each R^1 may be the same or different, however the bis-silyl aminosilane(s) is hydrolyzed in the solution such that at least a portion (and preferably all or substantially all) of the non-hydrogen R^1 groups are replaced by a hydrogen atom. Preferably, each R^1 is individually chosen from the group consisting of: hydrogen, ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.

Each R^2 in the aminosilane(s) may be a substituted or unsubstituted aliphatic group, or a substituted or unsubstituted aromatic group, and each R^2 may be the same or different. Preferably, each R^2 is chosen from the group consisting of: C_1 - C_{10} alkylene, C_1 - C_{10} alkenylene, arylene, and alkylarylene. More preferably, each R^2 is a C_1 - C_{10} alkylene (particularly propylene).

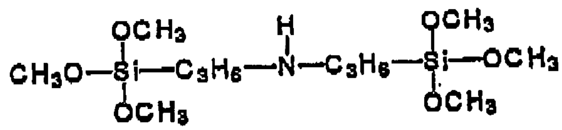
X may be:

wherein each R^3 may be a hydrogen, a substituted or unsubstituted aliphatic group, or a substituted or unsubstituted aromatic group, and each R^3 may be the same or different. Preferably, each R^3 is chosen from the group consisting of hydrogen, C_1 - C_6 alkyl and C_1 - C_6 alkenyl. More preferably, each R^3 is a hydrogen atom.

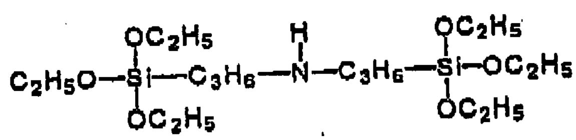
Finally, R^4 in the aminosilane(s) may be a substituted or unsubstituted aliphatic group, or a substituted or unsubstituted aromatic group. Preferably, R^4 is chosen from the group consisting of: C_1 - C_{10} alkylene, C_1 - C_{10} alkenylene, arylene, and alkylarylene. More preferably, R^4 is a C_1 - C_{10} alkylene (particularly ethylene).

Particularly preferred bis-silyl aminosilanes which may be used in the present invention include:

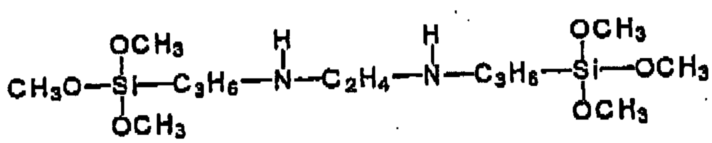
bis-(trimethoxysilylpropyl)amine (which is sold under the tradename A-1170 by Witco):



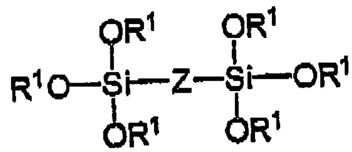
bis-(triethoxysilylpropyl)amine:



and bis-(triethoxysilylpropyl)ethylene diamine:

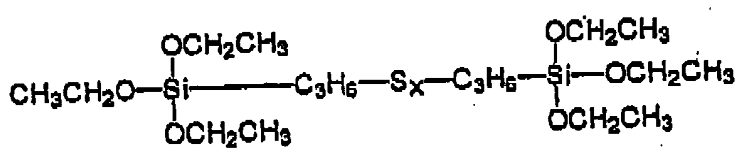


The preferred bis-silyl polysulfur silanes which may be employed in the present invention include:



wherein each R^1 is as described before. Once again the polysulfur silane(s) is hydrolyzed in the treatment solution such that at least a portion (and preferably all or substantially all) of the non-hydrogen R^1 groups are replaced by a hydrogen atom. Z is —Q—S_x—Q—, wherein each Q is an aliphatic (saturated or unsaturated) or aromatic group, and x is an integer of from 2 to 10. Q within the bis-functional polysulfur silane can be the same or different. In a preferred embodiment, each Q is individually chosen from the group consisting of: C_1 - C_6 alkyl (linear or branched), C_1 - C_6 alkenyl (linear or branched), C_1 - C_6 alkyl substituted with one or more amino groups, C_1 - C_6 alkenyl substituted with one or more amino groups, benzyl, and benzyl substituted with C_1 - C_6 alkyl.

Particularly preferred bis-silyl polysulfur silanes include bis-(triethoxysilylpropyl) sulfides having 2 to 10 sulfur atoms. Such compounds have the following formula:



wherein x is an integer of from 2 to 10. One particularly preferred compound is bis-(triethoxysilylpropyl) tetrasulfide (also referred to as bis-(triethoxysilylpropyl) sulfane, or "TESPT"). Commercially-available forms of TESPT (such as A-1289, available from Witco), however, are actually mixtures of bis-(triethoxysilylpropyl) sulfides having 2 to 10 sulfur atoms. In other words, these commercially-available forms of TESPT have a distribution of sulfide chain lengths, with the

S_3 and S_4 sulfides predominating. Thus, the scope of the present invention includes silane solutions containing mixtures of bis-silyl polysulfur silanes, either alone or in combination with one or more bis-silyl aminosilanes.

As mentioned above, the aminosilane(s) and the polysulfur silanes in the solutions of the present invention are at least partially, and preferably are substantially fully hydrolyzed in order to facilitate the bonding of the silanes to the metal surface and to each other. During hydrolysis, the non-hydrogen R^1 groups are replaced by a hydrogen atom. Hydrolysis of the silanes may be accomplished, for example, by merely mixing the silanes in water, and optionally including a solvent (such as an alcohol) in order to improve silane solubility and solution stability. Alternatively, the silanes may first be dissolved in a solvent, and water then added to accomplish hydrolysis. In order to accelerate silane hydrolysis and avoid silane condensation during hydrolysis, the pH may be maintained below about 10, more preferably in the preferred application pH ranges described previously. The pH may be adjusted, for example, by the addition of a compatible organic acid, as described previously. Some silanes provide the desired pH when mixed with water alone, and for these silanes pH adjustment may not be needed to accelerate silane hydrolysis.

It should be noted that the various silane concentrations discussed and claimed herein are all defined in terms of the ratio between the amount (by volume) of unhydrolyzed silane(s) employed to prepare the treatment solution (i.e., prior to hydrolyzation), and the total volume of treatment solution components (i.e., bis-silyl aminosilanes, bis-silyl polysulfur silanes, water, optional solvents and optional pH adjusting agents). In the case of aminosilane(s), the concentrations herein (unless otherwise specified) refer to the total amount of unhydrolyzed aminosilanes employed, since multiple aminosilanes may optionally be present. The polysulfur silane(s) concentrations herein are defined in the same manner.

As for the concentration of hydrolyzed silanes in the silane solution, beneficial results will be obtained over a wide range of silane concentrations and ratios. It is preferred, however, that the solution have at least about 0.1%

silanes by volume, wherein this concentration refers to the total concentration of bis-silyl aminosilane(s) and/or bis-silyl polysulfur silane(s) in the silane solution. The optimum silane concentration will vary depending upon the intended use. For example, higher concentrations of silanes may be effectively employed when the silane coating is to be used for corrosion protection only. More preferably, particularly when the silane solution is to be used for improving the adhesion of an electrocoat or other polymer coating, the solution has between about 0.1% and about 10% silanes by volume. When bis-silyl aminosilane(s) is employed without a bis-silyl polysulfur silane, the most preferred concentration of bis-silyl aminosilane is between about 0.5% and about 3% by volume. When bis-silyl polysulfur silane(s) is employed without a bis-silyl aminosilane, the most preferred concentration of bis-silyl polysulfur silane is between about 3% and about 7% by volume. When both a bis-silyl aminosilane and a bis-silyl polysulfur silane are present in the solution, and the solution is to be used for improving the adhesion of an electrocoat, the total silane concentration is most preferably between about 1% and about 3%.

When both bis-silyl aminosilane(s) and bis-silyl polysulfur silane(s) are employed, a wide range of silane ratios may also be employed. Thus, the present invention is not limited to any particular range of silane ratios. It is preferred, however, that the ratio of bis-silyl aminosilane(s) to bis-silyl polysulfur silane(s) in the silane solution is between about 1:99 and about 99:1. More preferably, particularly when the silane solution is to be applied to cold rolled steel, this ratio is between about 3:1 and about 99:1. Even more preferably, this ratio is between about 3:1 and about 9:1.

As reported in Application Serial No. 09/356,912, titled *Silane Coatings for Bonding Rubber to Metals*, which names Wim J. van Ooij, Senthil K. Jayaseelan and Eric A. Mee as inventors, which was filed on July 19, 1999, and the disclosure of which is incorporated herein by way of reference, the silane solutions of the present invention having both a bis-silyl aminosilane and a bis-silyl polysulfur silane also provide excellent adhesion to rubbers (particularly sulfur-cured rubbers). As reported in that application, and as incorporated

herein by way of reference, silane solutions for improving rubber bonding preferably have a ratio of bis-silyl aminosilane(s) to bis-silyl polysulfur silane(s) of between about 1:10 and about 10:1, most preferably between about 1:3 and about 1:1. In addition, the particularly preferred application pH for silane coatings used to improve rubber adhesion is between about 4 and about 7.

Since the solubility in water of some silanes suitable for use in the present invention may be limited (particularly the polysulfur silane), the treatment solution may optionally include one or more solvents (such as an alcohol) in order to improve silane solubility. Particularly preferred solvents include: methanol, ethanol, propanol and isopropanol. When a solvent is added, the amount of solvent employed will depend upon the solubility of the particular silanes employed (as well as their concentrations). Thus, when a solvent is used, the ratio of water to solvent may be between about 1:99 and about 99:1, more preferably between about 1:1 and about 1:20.

The method of preparing the silane solution is very simple. The unhydrolyzed silanes, water, solvent (if needed), and a small amount of acid (if pH adjustment is needed) are combined with one another. The solution is then stirred at room temperature in order to hydrolyze the silanes. The hydrolysis may take up to several hours to complete, and its completion will be evidenced by the solution becoming clear. In the case of bis-silyl polysulfur silanes, hydrolysis may be allowed to proceed for several days (such as 3 or 4 days) for optimal performance. When mixtures of bis-silyl aminosilane(s) and bis-silyl polysulfur silane(s) are used, it is preferred that the aminosilanes and polysulfur silanes are separately hydrolyzed in the same manner (including aging of the hydrolyzed polysulfur silane for 3-4 days or longer). As mentioned previously, the polysulfur silane may be prepared as an emulsion, with no solvent (other than water). The two solutions are then mixed together prior to coating of the metal substrate, and it is preferred that the two silane solutions are mixed with one another immediately prior to the coating of the metal substrate.

It should be understood that ceramic or glass substrates may be treated, with any of the silane treatment compositions of any aspect of the present invention, in an analogous way to the treatment of a metal substrate.

The metal surface to be coated with the solution of the present invention may be solvent and/or alkaline cleaned by techniques well-known to those skilled in the art prior to application of the silane solution of the present invention. The silane solution (prepared in the manner described above) is then applied to the metal surface (i.e., the sheet is coated with the silane solution) by, for example, dipping the metal into the solution (also referred to as "rinsing"), spraying the solution onto the surface of the metal, or even brushing or wiping the solution onto the metal surface. Various other application techniques well-known to those skilled in the art may also be used. When the preferred application method of dipping is employed, the duration of dipping is not critical, as it generally does not significantly affect the resulting film thickness. It is merely preferred that whatever application method is used, the contact time should be sufficient to ensure complete coating of the metal. For most methods of application, a contact time of at least about 2 seconds, and more preferably at least about 5 seconds, will help to ensure complete coating of the metal.

After coating with the silane solution of the present invention, the metal substrate may be air-dried at room temperature, or, more preferably, placed into an oven for heat drying. Preferable heated drying conditions include temperatures between about 20°C and about 200°C with drying times of between about 30 seconds and about 60 minutes (higher temperatures allow for shorter drying times). Temperatures above about 200°C should be avoided, except in the case of aluminum substrates. More preferably, heated drying is performed at a temperature of at least about 100°C, for a time sufficient to allow the silane coating to dry. While heated drying is not necessary to achieve satisfactory results (particularly in the case of silane solutions containing only a polysulfur silane), it will reduce the drying time thereby lessening the likelihood of the formation of white rust during drying. Once dried, the treated metal may be shipped to an end-user, or stored for later use.

The coatings of the present invention provide significant corrosion protection, even without being electrocoated. In addition, the coatings of the present invention provide corrosion resistance during both shipping and storage prior to electrocoating. More importantly, this silane coating need not be removed prior to electrocoating. Thus, the end-user (such as an automotive manufacturer) may electrocoat a second coating (such as a primer, a paint, or other protective or decorative coating) directly on top of the silane coating without additional treatment (such as the application of a phosphate conversion coating). The silane coatings of the present invention not only provide a surprisingly high degree of adhesion to the electrocoating, but also prevent delamination and underpaint corrosion even if a portion of the base metal is exposed to the atmosphere.

The silane coatings of the present invention may be used beneath either cathodic or anodic electrocoat materials, particularly cathodic electrocoats used in the automotive industry. Cathodic (or cationic) electrocoat materials are deposited as a coating on the cathode during an electrocoating process. Therefore, when a cathodic coating is applied by electrocoating, the workpiece (i.e., the metal substrate previously coated with the silane solution) becomes the cathode in the electrocoat cell. During the cathodic electrocoating process, the pH of the cathode (i.e., the metal substrate) increases sharply to about 10-12. The silane coatings of the present invention, however, are not only electrically conductive (as is required for proper electrocoating to take place), but also are resistant to alkali. Therefore, the silane coatings of the present invention allow for the formation of an excellent, high-build electrocoat film (i.e., coating).

The electrocoating process may be accomplished using apparatus and methods well-known to those skilled in the art. In fact, silane coated metal substrates prepared in accordance with the present invention may be electrocoated in the same manner as metal substrates which have been treated with phosphate conversion coatings. Suitable electrocoat materials include cathodic epoxy-urethane electrocoats such as ED-5000 (available from PPG Industries) or Powercron 641 (also available from PPG Industries). The

electrocoat may be applied by standard electrocoating techniques known to those skilled in the art.

EXAMPLES

The examples below demonstrate some of the superior and unexpected results obtained by employing the methods of the present invention. Unless otherwise noted, the various silane solutions described in the following examples were prepared by mixing the indicated silane(s) with water, solvent (ethanol), and acetic acid (if needed to provide the indicated pH during solution preparation). In instances wherein both a bis-silyl aminosilane and a bis-silyl polysulfur silane were employed, the silanes were first hydrolyzed separately in a solution of water and solvent, and the hydrolyzed silane solutions were then mixed to form the final silane solution composition in indicated. The silane solutions were hydrolyzed for at least 24 hours prior to application. The indicated metal substrates were solvent-cleaned, alkaline-cleaned, water rinsed, then dipped into the silane solution for approximately 1 minute, and then (unless otherwise indicated) dried at 100°C for about 5-10 minutes. After application of the silane coating, the samples were then cathodically electrocoated with ED-5000 using standard electrocoating conditions (250-300 volts, at room temperature, for about 5 minutes). After electrocoating, each sample was baked at 350°F for about 20 minutes.

As mentioned previously, the silane coatings of the present invention also provide improved corrosion protection, even without subsequent electrocoating, and provide adhesion to other polymer layers (such as non-electrocoat paints, rubbers and adhesives). Applicants' testing has shown that the silane coatings of the present invention provide improved corrosion protection and improved adhesion to a variety of paints and paint systems, including polyester, polyurethane, epoxy and acrylic paints (or combinations thereof). These paints can be water-borne, solvent-based or even powder paints. Thus, the present application is not limited to silane coatings for improving electrocoat adhesion.

<u>Example 1</u>

As shown in the table which follows, corrosion performance of electrocoated metal substrates having a silane undercoating in accordance with the present invention were compared to untreated metals and metals treated with a conventional phosphate conversion coating. Electrochemical impedance spectroscopy (EIS) was used to evaluate corrosion protection. In EIS testing, the polarization resistance, R_P, provides a measure of the corrosion resistance, with larger values of R_P, indicating better corrosion resistance. In the examples provided in the table below, the A-1170 silane solutions comprised 2 parts silane (by volume), 48 parts water, and 50 parts ethanol. Unless otherwise noted, the pH of the silane solutions was also adjusted to about 8 during solution preparation. For solutions containing 5% A-1289, the solution further comprised 5% water and 90% ethanol. In addition, panels coated with solutions containing A1289 (with no A1170) were dried at room temperature, rather than baked.

SAMPLE	R_p (in Ohms) After 8 weeks in 3% NaCl, pH 6	R_p (in Ohms) After 8 weeks in 3% NaCl, pH 3
EGS		
Alkaline-Cleaned only	1.19×10^{9}	9.96×10^{8}
Phosphated	3.31×10^{10}	3.25×10^{5}
A-1289 (5%)	2.96×10^{9}	1.46×10^{8}
A-1170 (2%)	1.29×10^{10}	5.69×10^{9}
HDG		
Alkaline-Cleaned only	6.78×10^{8}	9.7×10^{10}
Phosphated	6.69×10^{9}	8.75×10^{5}
A-1170 (2%)	3.60×10^{10}	2.75×10^{11}
CRS		
Alkaline-Cleaned only	4.63×10^{9}	2.75×10^{8}
Phosphated	5.59×10^{9}	1.44×10^{6}

SAMPLE	R_p (in Ohms) After 8 weeks in 3% NaCl, pH 6	R_p (in Ohms) After 8 weeks in 3% NaCl, pH 3
A-1289 (5%)	1.47×10^{11}	—
Aluminum Alloy (Al6061)		
Alkaline-Cleaned only	1.37×10^{11}	9.8×10^{7}
Phosphated	3.48×10^{10}	3.45×10^{10}
A-1170 (2%)	1.45×10^{11}	3.23×10^{11}

A-1170 = bis-(trimethoxysilylpropyl) amine
A-1289 = bis-(triethoxysilylpropyl) tetrasulfide

Example 2

Additional samples were prepared in the manner described above in Example 1. The solutions included equal parts silane(s) and water (by volume), with the remainder being ethanol (e.g., 2% UPS, 2% water, 96% ethanol). Unless otherwise noted, panels coated with solutions containing only A1289 were dried at room temperature, while panels coated with the other silane solutions were dried at 100°C for about 5-10 minutes prior to electrocoating. The pH of the silane solutions was 8, unless otherwise noted. It should also be pointed out that the natural pH of the A1289 solutions was about 4.5 to about 5 (without pH adjustment). In order to measure creepage, which in turn is indicative of the degree of paint adhesion and corrosion protection, a scribe was produced in electrocoated panels. The scribe was sufficiently deep to expose the base metal. The scribed panels were then subjected to a GM SCAB creep test, an accelerated corrosion test involving cycles of salt spray, humidity exposure (60°C and 85% RH) and drying over a 4 week period. After completion of the test period, a piece of adhesive tape was secured atop each scribe and then pulled off of the panel. The average

width of the area of electrocoat delamination was then measured for each panel, and the following results were obtained:

Sample	Creep
EGS	
Alkaline-cleaned only	6.0 ± 1.5
Phosphated	Negligible delamination*
UPS (2.0%, pH=6)**	7.00 ± 3.32
UPS (1.5%, pH=6)	9.9 ± 4.1
UPS (1.0%, pH=6)	7.11 ± 1.85
UPS (0.5%, pH=6)	10.0 ± 2.40
VS (2.0%, pH=4)	4.75 ± 2.22
VS (1.5%, pH=4)	5.13 ± 1.54
VS (1.0%, pH=4)	6.5 ± 2.75
VS (0.5%, pH=4)	4.0 ± 2.87
SAAPS (2.0%, pH=4)	5.11 ± 3.60
SAAPS (1.5%, pH=4)	3.63 ± 2.12
SAAPS (1.0%, pH=4)	7.38 ± 2.32
SAAPS (0.5%, pH=4)	6.13 ± 3.48
A-1170 (2.0%, pH=5)	2.86 ± 2.20
A-1170 (1.5%, pH=5)	4.38 ± 4.77
A-1170 (1.0%, pH=5)	3.33 ± 1.41
A-1170 (0.5%, pH=5)	8.63 ± 2.91
A-1170 (2.0%, pH=8)	Negligible delamination
A-1289 (5%, pH 4.5 - 5)	Negligible delamination
HDG	
Alkaline-cleaned only	4.7 ± 2.6
Phosphated	Negligible delamination

Sample	Creep
A-1170 (5%, dried at room temperature)	Negligible delamination
A-1170 (2%)	Negligible delamination
A-1289 (pH 4.5 - 5)	Negligible delamination
CRS	
Alkaline-cleaned only	27.0 ± 10.1
Phosphated	3.5 ± 0.7
A-1170	18.6 ± 5.4
A-1289 (5%, pH 4.5 - 5)	19.5 ± 3.6
A-1170 + A-1289 (9:1 mixture; 2% total silanes in the silane solution; pH 6; dried at room temperature)	6.5 ± 1.7
Al alloys (Al 6061 & Al 6111)	
Alkaline-cleaned only	Negligible delamination
Phosphated	Negligible delamination
A-1170 (5%, dried at room temperature)	Negligible delamination
A-1170 (5%)	Negligible delamination

* Average Creep <0.5 mm
** UPS panels were subjected to the humidity for 8 weeks
UPS = γ-ureidopropyltrialkoxysilane (γ-UPS)
SAAPS = N-[2-(vinylbenzylamino)-ethyl]-3-aminopropyltrimethoxysilane
VS = vinyltrimethoxysilane
A-1170 = bis-(trimethoxysilylpropyl) amine
A-1289 = bis-(triethoxysilylpropyl) tetrasulfide

As noted in the above table, both A-1289 and A-1170 provided negligible delamination on metals other than CRS. On CRS, the A-1289 and A-1170 solutions performed marginally better than the blank sample (i.e.,

alkaline-cleaned only), but significantly worse than the phosphated sample. However, the silane solution containing a mixture of A-1289 and A-1170 performed remarkably better than either silane alone, and nearly as well as the phosphated sample.

Example 3

were also tested by scribing the sample, and then immersing the scribed panels in 3% NaCl for 5 days at 60°C. Creep was then measured in the

width of the area of electrocoat delamination was then measured for each panel, and the following results were obtained:

Sample	Creep
EGS	
Alkaline-cleaned only	6.0 ± 1.5
Phosphated	Negligible delamination*
UPS (2.0%, pH=6)**	7.00 ± 3.32
UPS (1.5%, pH=6)	9.9 ± 4.1
UPS (1.0%, pH=6)	7.11 ± 1.85
UPS (0.5%, pH=6)	10.0 ± 2.40
VS (2.0%, pH=4)	4.75 ± 2.22
VS (1.5%, pH=4)	5.13 ± 1.54
VS (1.0%, pH=4)	6.5 ± 2.75
VS (0.5%, pH=4)	4.0 ± 2.87
SAAPS (2.0%, pH=4)	5.11 ± 3.60
SAAPS (1.5%, pH=4)	3.63 ± 2.12
SAAPS (1.0%, pH=4)	7.38 ± 2.32
SAAPS (0.5%, pH=4)	6.13 ± 3.48
A-1170 (2.0%, pH=5)	2.86 ± 2.20
A-1170 (1.5%, pH=5)	4.38 ± 4.77
A-1170 (1.0%, pH=5)	3.33 ± 1.41
A-1170 (0.5%, pH=5)	8.63 ± 2.91
A-1170 (2.0%, pH=8)	Negligible delamination
A-1289 (5%, pH 4.5 - 5)	Negligible delamination
HDG	
Alkaline-cleaned only	4.7 ± 2.6
Phosphated	Negligible delamination

Sample	Creep
A-1170 (5%, dried at room temperature)	Negligible delamination
A-1170 (2%)	Negligible delamination
A-1289 (pH 4.5 - 5)	Negligible delamination
CRS	
Alkaline-cleaned only	27.0 ± 10.1
Phosphated	3.5 ± 0.7
A-1170	18.6 ± 5.4
A-1289 (5%, pH 4.5 - 5)	19.5 ± 3.6
A-1170 + A-1289 (9:1 mixture; 2% total silanes in the silane solution; pH 8; dried at room temperature)	6.5 ± 1.7
Al alloys (Al 6061 & Al 6111)	
Alkaline-cleaned only	Negligible delamination
Phosphated	Negligible delamination
A-1170 (5%, dried at room temperature)	Negligible delamination
A-1170 (5%)	Negligible delamination

* Average Creep <0.5 mm
** UPS panels were subjected to the humidity for 8 weeks
UPS = γ-ureidopropyltrialkoxysilane (γ-UPS)
SAAPS = N-[2-(vinylbenzylamino)-ethyl]-3-aminopropyltrimethoxysilane
VS = vinyltrimethoxysilane
A-1170 = bis-(trimethoxysilylpropyl) amine
A-1289 = bis-(triethoxysilylpropyl) tetrasulfide

As noted in the above table, both A-1289 and A-1170 provided negligible delamination on metals other than CRS. On CRS, the A-1289 and A-1170 solutions performed marginally better than the blank sample (i.e.,

alkaline-cleaned only), but significantly worse than the phosphated sample. However, the silane solution containing a mixture of A-1289 and A-1170 performed remarkably better than either silane alone, and nearly as well as the phosphated sample.

Example 3

Electrocoated samples prepared in the manner described in Example 2 were also tested by scribing the sample, and then immersing the scribed panels in 3% NaCl for 5 days at 60°C. Creep was then measured in the manner described above in Example 2.

Sample	Creep (mm)
EGS	
Phosphated	1.2 ± 0.9
Blank	22.6 ± 10.1
A-1170 (0.5%)	5.1 ± 2.1
A-1170 (2.0%)	Negligible delamination
A-1170 (2.0%, baked at 205°C for 30 min.)	5.1 ± 2.8
A-1170 (3.0%)	3.9 ± 1.1
A-1170 (4.0%)	6.2 ± 4.3
A-1170 (5.0%)	7.0 ± 1.2
A-1170 (2.0%, dried at room temp.)	3.4 ± 1.9
A-1170 (5.0%, dried at room temp.)	11.5 ± 4.5
A-1289 (5%, pH 4.5 - 5)	1 ± 0.8
A-1289 (5%, pH 4.5 - 5, baked at 205°C for 30 min.)	2.1 ± 1.6
A-1289 (2%, pH 4.5 - 5)	12.1 ± 6.6
A-1170 + A-1289 (9:1 mixture; 2% total silanes in the silane solution; pH=8; dried at room temperature)	3.7 ± 1.1

Sample	Creep (mm)
A-1170 + A-1289 (9:1 mixture; 2% total silanes in the silane solution; pH=8; baked at 205°C for 30 min.)	5.5 ± 2.2
HDG	
Blank	Complete delamination
Phosphated	Negligible delamination
A-1289 (2%, pH 4.5 - 5)	3.8 ± 0.4
Sulfane (5%, pH 4.5 - 5)	Negligible delamination
A-1170 (2%)	Negligible delamination
A-1170 (5%)	Negligible delamination
A-1170 (5%, dried at room temp.)	Negligible delamination
CRS	
Blank	6.8 ± 1.7
Phosphated	Negligible delamination
A-1170 (2%)	2.9 ± 1.6
A-1170 (2%, pH=5)	5 ± 1.7
A-1289 (5%, pH 4.5 - 5)	Complete delamination
A-1170 + A-1289 (9:1 mixture; 2% total silanes in the silane solution; pH=8; dried at room temp.)	3.5 ± 2.0
A-1170 + A-1289 (9:1 mixture; 2% total silanes in the silane solution; pH=8; baked at 205°C for 30 min.)	Complete delamination
A-1170 + A-1289 (4:1 mixture; 2% total silanes in the silane solution; pH=8)	2.5 ± 0.7
A-1170 + A-1289 (9:1 mixture; 2% total silanes in the silane solution; pH=6)	4.0 ± 1.5

Sample	Creep (mm)
A-1170 + A-1289 (3:1 mixture; 2% total silanes in the silane solution; pH=6)	6.8 ± 2.9
Two-step treatment: BTSE (1%, pH=5, blown dry); followed by APS (1%, natural pH)	Negligible delamination
Al alloys (Al 6061 & Al 6111)	
Blank	Negligible delamination
Phosphated	Negligible delamination
A-1170 (5%)	Negligible delamination
A-1170 (5%, dried at room temp.)	Negligible delamination

Example 4

In order to further examine electrocoat adhesion to the silane coatings of the present invention, panels were coated with a silane solution in the manner described in Example 2 and then electrocoated. The electrocoated panels were then immersed in N-methyl pyrrolidone (NMP) at 60°C and the time until delamination of the electrocoat was measured.

Sample	NMP Retention Time (minutes)
CRS	
Alkaline-cleaned only	<1
Phosphated	37
A-1170 + A-1289 (9:1 mixture; 2% total silanes in the silane solution; pH 8; dried at room temperature)	>24 hours with no delamination
Al 6111	
Alkaline-cleaned only	8.9
Phosphated	79

Sample	NMP Retention Time (minutes)
A-1170 (2.0%, pH 8.5)	>24 hours with no delamination
EGS	
Alkaline-cleaned only	<2
Phosphated	30
A-1289 (2.5%, pH 4.5 - 5, dried at room temp.)	25
A-1289 (5%, pH 4.5 - 5, dried at room temp.)	~450
A-1170 (5%, pH 8, dried at room temp.)	>6 hrs (underwent some attack, but not complete delamination)
A-1170 (2%, pH 8)	>24 hrs

Example 5

In order to examine the corrosion protection provided by the silane compositions of the present invention, silane coatings were applied to pure aluminum panels in the manner described in Example 2. The panels were not electrocoated. After drying, the silane coated panels were then placed into a 3% NaCl solution for 192 hours. Corrosion was evaluated qualitatively, and the results are shown below.

Silane Solution	pH	Drying	Surface Observation
Blank	N/A	---	large size pits, distributed uniformly
A1170 (5%)	8	dried at room temperature	small pits, distributed uniformly
A1289 (5%)	8	dried at room temperature	almost original appearance

Silane Solution	pH	Drying	Surface Observation
A-1170 + A-1289 (1:1 mixture, 10% total silanes in the silane solution)	8	dried at room temperature	almost original appearance

As shown in the above table, the mixture of hydrolyzed A1170 and A1289 provided excellent corrosion protection (superior to hydrolyzed A1170 alone, and at least equivalent to hydrolyzed A1289 alone). Thus, the silane solutions and methods of the present invention not only provide superior adhesion to electrocoats, but also provide corrosion protection (with or without a polymer layer over the silane coating).

Example 6

In order to evaluate the adhesion to paint provided by the hydrolyzed silane solutions of the present invention, samples of hot-dipped galvanized steel were coated with hydrolyzed silane solutions prepared and applied in the manner described in Example 2. The treated panels were then painted with a polyester powder paint in the usual fashion. In order to measure creepage, which in turn is indicative of the degree of paint adhesion and corrosion protection, a scribe was produced in the painted panels. The scribe was sufficiently deep to expose the base metal. The scribed panels were then subjected to a salt spray for 1000 hours (ASTM B-117. After completion of the test period, a piece of adhesive tape was secured atop each scribe and then pulled off of the panel. The average width of the area of paint delamination was then measured for each panel, and the following results were obtained:

Silanes	Drying Conditions	Scribe Creep (mm)
A-1170, 2%, pH=8	100°C, 10 minutes	13.5 ± 8.5
	dried at room temp.	6.72 ± 3.1
A-1289, 5%, pH=8	100°C, 10 minutes	14.4 ± 8.5
	dried at room temp.	15.1 ± 9.7
A-1170 + A-1289, 2% each (1:1), pH=8	100°C, 10 minutes	13.2 ± 9.9

Silanes	Drying Conditions	Scribe Creep (mm)
	dried at room temp.	12.6 ± 7.0
Blank (alkaline cleaned only)	---	Completely delaminated

Example 7

Samples of GALVALUME® were coated with hydrolyzed silane solutions, and painted with a polyester powder paint. Scribe creep was then measured after salt spray exposure in the manner described in Example 6.

Silanes	Curing Condition	Scribe Creep (mm)
A-1170, 2%, pH=8	100°C, 10 minutes	1.2 ± 2.2
	dried at room temp.	1.2 ± 2.2
A-1289, 5%, pH=8	100°C, 10 minutes	negligible delamination
	dried at room temp.	negligible delamination
A-1170 + A-1289, 2% each (1:1), pH=8	100°C, 10 minutes	negligible delamination
	dried at room temp.	negligible delamination
Blank (alkaline cleaned only)	---	Completely delaminated

As the above examples demonstrate, the silane solutions of the present invention also provide adhesion to other types of paint systems (in addition to electrocoats).

Example 8

In order to examine the corrosion protection provided by the silane compositions of the present invention on magnesium alloys, a silane coating was applied to a panel of magnesium alloy AZ31-B in the manner described previously. It should be noted that both the silane coated panel, as well as the uncoated control, were first cleaned in a chromic acid solution in order to remove the graphite layer present on the panels. The silane solution comprised a hydrolyzed mixture of 2% A-1170 and 5% A-1289. The resulting silane film was cured at 160°C for 40 minutes. The panels were not

electrocoated. The silane coated magnesium panel, as well as an uncoated magnesium panel, were then subjected to EIS in order to evaluate corrosion protection. The corrosion rate for the untreated panel was 7500 mpy, while the silane treated panel exhibited a corrosion rate of only 5 mpy. Thus, the silane solutions and methods of the present invention provide corrosion protection on magnesium alloys (with or without a polymer layer over the silane coating).

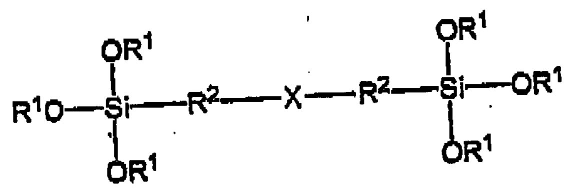
Claims

1. A method of electrocoating a metal substrate, comprising:

(a) applying a first coating of a silane solution onto the metal substrate, said silane solution comprising at least one silane which has been at least partially hydrolyzed, said silane chosen from the group consisting of bis-silyl aminosilanes and bis-silyl polysulfur silanes; and

(b) electrocoating a second coating onto said first coating.

2. The method of claim 1, wherein said at least one silane comprises:

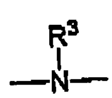


wherein:

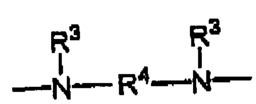
each R^1 is individually chosen from the group consisting of: hydrogen, C_1 - C_{24} alkyl and C_2 - C_{24} acyl;

each R^2 is individually chosen from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups; and

X is either:



or



wherein each R^3 is individually chosen from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and

R^4 is chosen from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups.

3. The method of claim 2, wherein each R^1 is individually chosen from the group consisting of: hydrogen, ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.

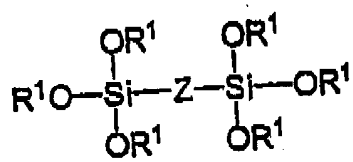
4. The method of claim 2, wherein each R^2 is individually chosen from the group consisting of: C_1 - C_{10} alkylene, C_1 - C_{10} alkenylene, arylene, and alkylarylene.

5. The method of claim 2, wherein each R^3 is individually chosen from the group consisting of: hydrogen, C_1 - C_6 alkyl and C_1 - C_6 alkenyl.

6. The method of claim 2, wherein R^4 is chosen from the group consisting of: C_1 - C_{10} alkylene, C_1 - C_{10} alkenylene, arylene, and alkylarylene.

7. The method of claim 1, wherein said bis-silyl aminosilane is chosen from the group consisting of: *bis*-(trimethoxysilylpropyl)amine, *bis*-(triethoxysilylpropyl)amine, and bis-(triethoxysilylpropyl)ethylene diamine.

8. The method of claim 1, wherein said at least one silane comprises:



wherein each R^1 is an alkyl or an acetyl group, and Z is $—Q—S_x—Q—$, wherein each Q is an aliphatic or aromatic group, and x is an integer of from 2 to 10.

9. The method of claim 8, wherein each R^1 is individually chosen from the group consisting of: hydrogen, ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.

10. The method of claim 8, wherein each Q is individually chosen from the group consisting of: C_1 - C_6 alkyl (linear or branched), C_1 - C_6 alkenyl (linear or branched), C_1 - C_6 alkyl substituted with one or more amino groups, C_1 - C_6 alkenyl substituted with one or more amino groups, benzyl, and benzyl substituted with C_1 - C_6 alkyl.

11. The method of claim 8, wherein said bis-functional polysulfur silane comprises a bis-(triethoxysilylpropyl) sulfide having 2 to 10 sulfur atoms.

12. The method of claim 11, wherein said at least one silane comprises bis-(triethoxysilylpropyl) tetrasulfide.

13. The method of any preceding claim, wherein said metal substrate is chosen from the group consisting of:

-a metal substrate having a zinc-containing coating;

-steel;

-aluminum;

-aluminum alloys;

-zinc;

-zinc alloys;

-magnesium;

-magnesium alloys;

-copper;

-copper alloys;

-tin; and

-tin alloys.

14. A method of treating a substrate, comprising:

(a) providing a substrate; and

(a) applying a coating of a silane solution onto the substrate, said silane solution comprising at least one bis-silyl aminosilane which has been at least partially hydrolyzed and at least one bis-silyl polysulfur silane which has been at least partially hydrolyzed.

15. The method according to claim 14, wherein the substrate is selected from the group consisting of metals, ceramics and glass.

16. The method of claim 14 or 15, wherein said bis-silyl aminosilane has the formula as defined in any of claims 2 to 7.

17. The method of claim 14, wherein said at least one bis-silyl polysulfur silane has the formula as defined in any of claims 8 to 12.

18. The method of claim 16, wherein said substrate is metal and is chosen from the group consisting of:

-a metal substrate having a zinc-containing coating;

-steel;

-aluminum;

-aluminum alloys;

-zinc;

-zinc alloys;

-magnesium;

-magnesium alloys;

-copper;

-copper alloys;

-tin; and

-tin alloys.

19. The method of any preceding claim, wherein the total concentration of silanes in said silane solution is between about 0.1% and about 10% by volume.

20. The method of any of claims 14 to 19, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane solution is between about 1:99 and about 99:1.

21. The method of claim 20, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane solution is between about 3:1 and about 99:1.

22. The method of claim 20, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane solution is between about 1:3 and about 1:1.

23. The method of any of claims 14 to 22, wherein said bis-silyl aminosilane is chosen from the group consisting of *bis*-(trimethoxysilylpropyl)amine, *bis*-(triethoxysilylpropyl)amine, and bis-(triethoxysilylpropyl)ethylene diamine, preferably *bis*-(trimethoxysilylpropyl)amine, and wherein said at least one bis-silyl polysulfur silane comprises bis-(triethoxysilylpropyl) tetrasulfide.

24. The method of any preceding claim, further comprising the step of applying a second coating onto said first coating.

25. The method of claim 24, wherein said second coating is selected from paint, adhesive, rubber and plastic.

26. The method of claim 24, wherein said second coating is plastic, wherein the plastic is selected from acrylic, polyester, polyurethane,

polyethylene, polyimide, polyphenylene oxide, polycarbonate, polyamide, epoxy, phenolic, acrylonitrile-butadiene-styrene, and acetal plastics.

27. The method of claim 24, wherein said second coating is rubber, wherein the rubber is selected from sulfur cured rubbers, nitrile rubbers, chloroprene rubbers, polyisoprenes, polybutadienes, sillicone rubbers (including fluorosilicone rubbers), acrylic rubbers and isoprene-acrylonitrile rubbers.

28. The method of claim 24, wherein said second coating is a paint and comprises an electrocoating.

29. The method of claim 28, wherein said second coating is selected from cathodic electrocoating and epoxy-urethane electrocoating.

30. A silane coated substrate made in accordance with the method of claim 14.

31. An electrocoated metal substrate made in accordance with the method of any preceding claim 1.

32. A silane solution comprising:

-at least one substantially hydrolyzed bis-silyl aminosilane; and

-at least one substantially hydrolyzed bis-silyl polysulfur silane.

33. The silane solution of claim 32, wherein said bis-silyl aminosilane has the formula as defined in any of claims 2 to 7.

34. The silane solution of claim 32, wherein said at least one bis-silyl polysulfur silane has the formula as defined in any of claims 8 to 12.

35. The silane solution of any of claims 32 to 34, wherein the total concentration of silanes in said silane solution is between about 0.1% and about 10% by volume.

36. The silane solution of any of claims 32 to 35, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane solution is between about 1:99 and about 99:1.

37. The silane solution of claim 36, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane solution is between about 3:1 and about 99:1.

38. The silane solution of claim 36, wherein the ratio of bis-silyl aminosilanes to bis-silyl polysulfur silanes in said silane solution is between about 1:3 and about 1:1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/03711

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D5/44 C09D183/14 C09D5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 August 2000	17/08/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Depijper, R

INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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